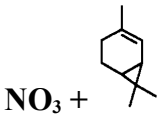
IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO3_VOC34

This data sheet last evaluated: June 2013; last change in preferred values: June 2013.



NO_3 + (2-carene) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.66 \pm 0.18) \times 10^{-11}$	298	Martínez et al., 1999	DF-LIF (a)
$1.4 \times 10^{-12} \exp[(741 \pm 190)/T]$	298-433		
Relative Rate Coefficients			
$(1.87 \pm 0.11) \times 10^{-11}$	295	Corchnoy and Atkinson, 1990	RR (b)
$(2.16 \pm 0.36) \times 10^{-11}$			

2-carene is 3,7,7-trimethyl-bicyclo[4.1.0]hept-2-ene.

Comments

(a) NO_3 radicals (6-30 × 10^{11} molecule cm^{-3}) generated from reaction of F atoms (made in a microwave discharge through F_2/He) with HNO_3. Flow tube was operated at ~1.33 mbar (1 Torr) He at 4 temperatures between 298 and 433 K. 2-carene was present at similar concentrations (1-3 fold) to NO_3. So that absolute NO_3 concentrations (derived by titration with tetramethylethene) were necessary to derive the rate coefficient.

(b) 6400 L Teflon chamber at 295 K and 980 mbar (735 Torr) of air. NO_3 was generated by the thermal decomposition of N_2O_5. 2-carene and either 2,3-dimethyl-2-butene or 2-methyl-2-butene (reference reactants) were monitored by GC to obtain rate constant ratios, $k(NO_3 + \text{2-carene}) / k(NO_3 + \text{2,3-dimethyl-2-butene}) = 0.377 \pm 0.063$ and $k(NO_3 + \text{2-carene}) / k(NO_3 + \text{2-methyl-2-butene}) = 2.00 \pm 0.12$. Using values of $k(NO_3 + \text{2-methyl-2-butene}) = 9.37 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003) and $k(NO_3 + \text{2,3-dimethyl-2-butene}) = 5.72 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003) the relative rates are converted to the absolute rate constants listed in the table. The value of $(1.87 \pm 0.11) \times 10^{-11}$ molecule cm^{-3} corresponds to the experiments in which 2-methyl-2-butene was used as reference.

Preferred Values

Parameter	Value	T/K

k /cm^3 molecule^{-1} s^{-1}	2.0×10^{-11}	298

Reliability

$\Delta \log k$	± 0.12	298

Comments on Preferred Values

The three determinations of the room temperature rate coefficient agree to within ~30 % and the preferred value of the room temperature rate coefficient is based on the relative rate studies. The temperature dependence observed by Martínez et al. (1999) requires validation before a recommendation can be made.

There are no product studies of this reaction, though the large rate constant indicates that the reaction proceeds mainly via addition of NO_3 across a double bond to form a chemically activated nitrooxyalkyl radical. At pressures found in the troposphere this adduct will undergo collisional stabilization prior to reaction with O_2 to form a nitrooxyalkyl peroxy radical or decompose to release NO_2. At atmospheric pressure the formation of the peroxy radical will generally dominate.

References

Atkinson, R., and Arey, J., Chem. Rev., 103, 4605-4638, 2003.

Corchnoy, S. B., and Atkinson, R., Env. Sci. Tech., 24, 1497-1502, 1990.

Martínez, E., Cabañas, B., Aranda, A., Martín, P., and Salgado, S., J. Atmos. Chem., 33, 265-282, 1999.